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THE ELECTRON SPIN RESONANCE SPECTRUM OF DIBENZENE CHROMIUM CATION

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ABSTRACT

The electron spin paramagnetic resonance of dibenzene chromium cation has been observed. Its center is at a value of g = 1.98. It shows eleven hyperfine components separated by 3.5 gauss. These are interpreted to be eleven of the thirteen components expected to result from the interaction of the twelve equivalent protons with the unpaired electron.

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Recently a discussion of the type of bonding involved in "sandwich" molecules has appeared in the literature.[1] The nuclear hyperfine splitting of an electron-spin resonance absorption in principle can be used to establish the electron spin density at the various magnetic nuclei in the molecule.[2] Accordingly, we have examined the spin resonance spectrum of the dibenzene chromium cation** with the objective of determining whether or not the odd electron is localized on the chromium or spread out over the whole π system.

The paramagnetic resonance spectrum of the cation in an aqueous solution (Fig. 1) was taken on a differentiating, transmission-cavity spectrometer operating at a frequency of 9.3 kmc./sec. The spectrum is symmetric and consists of approximately eleven barely resolved lines with a spacing of about 3.5 oersteds. The g value for the center of the pattern is 1.98 ± 0.01 as determined on the basis of $g = 2.0036$ for 1,1 diphenyl-2 picrylhydrazyl. Further dilution together with degassing of the sample failed to decrease the line width, while more concentrated solutions exhibited poorer resolution.

The fine structure appearing in the spin resonance spectrum is attributed to hyperfine interaction between the odd electron and the twelve equivalent protons on the benzene rings. Such an interaction would give rise to thirteen

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1 Craig, Maccoll, Nyholm, Orgel, and Sutton, J. Chem. Soc. 332 (1954).

2 S.I. Weissman, J. Chem. Phys. 22, 1135 (1954).

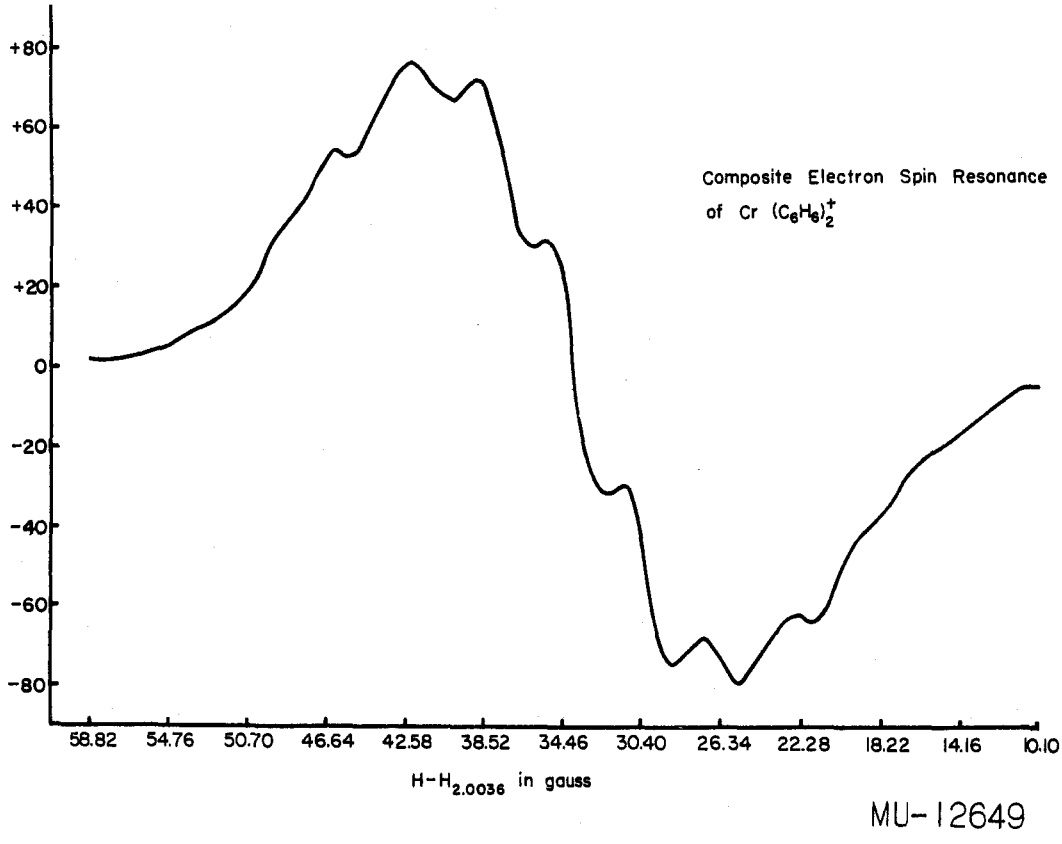

Fig. 1. Composite electron spin resonance of $Cr(C_6H_6)_2^+$.

equally spaced lines with the intensity ratios: 1 : 12:66: 220 : 495 : 792 : 924 : 792 : 495 : 220 : 66 : 12 : 1. At best, we have observed 11 lines. The failure to observe all 13 lines may be attributed to poor signal-to-noise ratio for the end lines of the spectrum. The only other magnetic nucleus in the molecules with appreciable abundance is Cr^{53} (9.5%) which has a nuclear spin of 3/2 and a small magnetic moment. We were not able to observe hyperfine splitting by this nucleus.

The fact that proton hyperfine structure is observable together with the fact that the observed g value is approximately the same as that obtained from chromium salts[3] indicates that the bonding between the benzene rings and the chromium atoms involves a deep-seated hybridization of the π orbitals of the rings and the d orbitals of the chromium atom. A similar conclusion about the bonding in coordination compounds has been drawn by Griffiths and Owen[4] in the case of the chlorine nuclear splitting in $IrCl_6^{--}$. A further case is the nitrogen hyperfine interaction of a copper unpaired electron in copper bisacetylacetonethylenediiminate.[5] As a measure of the apparent spin density of an aromatic odd electron at a proton nucleus, let us use the proton hyperfine splitting of benzene negative ion, in which we can be fairly confident that the odd electron occupies a π orbital. Weissman, Tuttle, and de Boer have found this splitting to be 3.75 oersted.[6] The fact that the total electron-spin density on the protons of chromium dibenzene cation is approximately twice that obtained for benzene negative ion seems inconsistent with the observed g value. This may be reconciled if one considers that the time spent by the electron on a proton is dependent upon carbon-hydrogen hybridization as well as on how the π electrons are involved in bonding.[7,8] The molecular orbital viewpoint of a covalent bond[1] between the chromium and the π system seems to us to be consistent with the above observations, particularly if this entails some distortion or modification of the orbitals used in the C-H bond.

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[3] K.D. Bowers and J. Owen, Repts. Progr. Phys. 18, 304 (1955).

[4] J.H.E. Griffiths and J. Owen, Proc. Royal Soc. A226, 96 (1954); see M. Tinkham, Proc. Royal Soc. A236, 549 (1956) for F interaction.

[5] R.D. Feltham, Thesis, to be published.

[6] Weissman, Tuttle, and de Boer, J. Phys. Chem., in press.

[7] S.I. Weissman, J. Chem. Phys. 25, 890 (1956).

[8] B. Venkataraman and G.K. Fraenkel, J. Chem. Phys. 23, 588 (1955).